COMPARISON OF THE PERFORMANCE OF WASHCOATING VARIATIONS FOR FISHER-TROPSCH SYNTHESIS IN A MICROCHANNEL REACTOR

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ABSTRACT

Interest in biomass based Fischer-Tropsch fuels is currently heightened due to a global focus on the need for biofuels. While Fischer-Tropsch technology could be considered mature with significant worldwide production based on natural gas or coal, the challenge now is to develop Fischer-Tropsch processes that are economic at the smaller scale necessitated by the limitations of a biomass supply chain. The reactor is one aspect of this process and is the focus of this research. A microchannel reactor has been constructed and the performance compared against a more traditional fixed bed reactor. The microchannel reactor is constructed by wire cutting of 0.2 mm 316ss shim to yield channel dimensions of 0.2 × 0.3 × 37 mm with 50 channels per shim. The reactor was washcoated with unsupported cobalt, cobalt on titania, and a combustion synthesis cobalt deposition method. Comparison was made to a simple cobalt on titania catalyst in a fixed bed reactor. The catalysts were compared at 210, 225 and 240°C. The simple unsupported cobalt washcoat catalyst had slightly higher productivity per unit catalyst of all catalysts tested in the microchannel reactor and was 32 to 40 times more effective than the fixed bed reactor over the temperature range tested and also more effective than similar catalyst in a batch slurry reactor. This shows the microchannel reactor system to have significant advantages in terms of catalyst utilization compared to traditional reactors.

INRODUCTION

While Fischer-Tropsch synthesis could be considered an established technology, the technology currently applies to large scale. With biomass as a feedstock the resource is far more dispersed requiring either large transportation distances to a larger plant, or to more localised smaller plants that maximise the available localised source of biomass. In New Zealand there are approximately 20 million m^3 of round wood harvested per year (Cox, 2008) of which there are significant quantities of wood waste left over from milling operations (SCION et al., 2007). The scenario proposed here is a combined heat, power, and liquid fuels plant on a wood processing site where the waste can be utilised (as well as supplementary feedstock from the region). This does necessitate, however, a scale of plant orders of magnitude smaller than traditional FT processes.

Microchannel reactor technology is seen as part of the solution to economically producing liquid fuels at smaller scale. Currently there is little commercial development of FT based microchannel technology, however, those attempting to make it a commercial endeavour do claim significant cost effectiveness at smaller scale compared to existing technology (Tonkovich et al., 2008). Research is becoming more prevalent in

the area of microreactors with at least one very good overview of the topic (Gavriilidis et al., 2002).

Microchannel reactors are seen as being very suitable for FT synthesis. The high rate of heat transfer available within a microreactor system is ideal for controlling the highly exothermic FT reaction. The scalability of microchannel reactors is also seen as a significant advantage, especially given the unconventional scale in question in this paper. Scale-up with micro-reactors is more a case of numbering up of either channels or reactor modules (Gavriilidis et al., 2002). This provides greater confidence in repeatability of lab scale results on a larger scale. A common question or objection to microchannel reactors is the high potential for plugging with particulates. In FT synthesis this problem is solved by pure virtue of the process – the catalyst requires a very clean syngas feed, therefore the prior rigorous cleanup steps have removed all particulate matter. There is the potential for coking in FT which would be detrimental in the small channels. However, coking is usually caused by higher temperature deviations (Steynberg and Dry, 2004), a difficulty that should not be associated with a microchannel reactor due to the high rates of heat transfer.

One of the challenges of microchannel reactors is the ability to appropriately load catalyst into the reactor. There are a number of papers on this subject although much literature involves coating microchannels (or monoliths and other microreactor shapes) outside of the reactor before assembly (Visconti et al., 2009, Pfeifer et al., 2005, Almeida et al., 2011). However, research investigating the addition of catalyst, post reactor assembly is deemed important as it is very likely full scale units will be permanently sealed to ensure reliability at the high operating pressures required for FT synthesis. This paper therefore investigates several types of catalyst washcoated into an assembled microchannel reactor. This research intentionally keeps the catalyst preparation method relatively simple. While some literature produces high performing catalysts through complex methods (Nagineni et al., 2005, Chin et al., 2005) , the aim of this research is to produce simple, cost effective reactor and catalyst systems at a smaller scale. Therefore complex and potentially difficult to repeat (at least at scale) methods, as well as precious metal promoters have been eliminated. The intention is to use this study as a base case to select the most effective catalyst for further washcoating and reactor optimisation to best suit a small scale biomass fed combined heat, power and liquid fuels plant. The most effective catalyst being the one which exhibits the highest activity and best selectivity to diesel range fuels.

EXPERIMENTAL

Reactor construction

The reactor was designed to be easily disassembled to allow investigation and replacement of the microchannel shims, while still able to seal at suitable pressures for Fischer-Tropsch Synthesis (20-30 bar). The reactor contains alternate feed shims and microchannel shims (Figure 1).

Fig. 1: Feed shim on left, microchannel shim on right

The shims were fabricated from 316ss with a thickness of 200 μm. The microchannels are 37mm long, 300 μm wide with 50 channels per shim. The shims were constructed by wire cutting. The channel width was partly dictated by the minimum possible width the wire cutting technology would allow. Wire cutting was chosen as it allowed mass manufacture via a stack of shims being cut at once, in turn producing excellent repeatability of dimensions and channel finish between each shim. This method was also selected because it was deemed to be a realistic method for larger scale manufacture (at least for larger lab scale or smaller pilot scale plants).

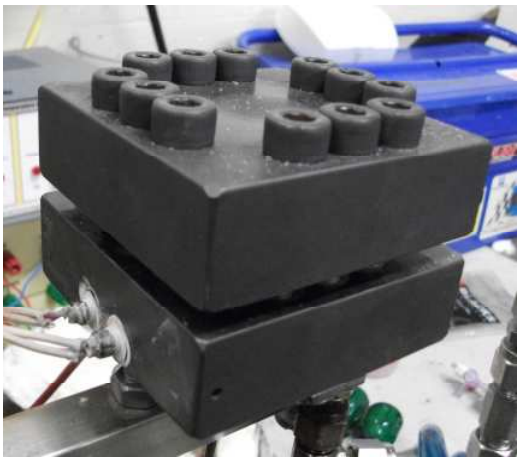

Fig. 2: Reactor installed in rig showing top and bottom plates and cartridge heaters. Reactor ports are underneath reactor and obscured from view

In order to provide adequate sealing substantial top and bottom sandwich plates were constructed from 25mm thick stainless tool steel (Stavax®) and hardened to prevent bowing (Figure 2). The thick plates also allowed the addition of cartridge heaters to control the temperature of calcination, reduction and FT synthesis.

The reactor is bolted together with 12 grade 12.9 M8 cap screws torqued to 25 ft-lb in a criss cross pattern. Gaskets were cut from aluminium foil. While other literature suggests this style of reactor will not hold significant pressure (Guillou et al., 2008) these steps allowed the reactor to seal up to the maximum testing pressure of 35 bar. Many reduction and calcination steps at 400°C removed the hardening from the Stavax® but reactor sealing remained adequate.

Rig setup

The trial rig used was a single stream system due to the use of pre-mixed gas (see Figure 3). The gas mix is 64% H_2, 32% CO and 4% N_2. The N_2 is used as a tracer gas to enable mass balance closure and error analysis. Upstream of the reactor an electronic mass flow meter measured the flow, while post the reactor and collection system a syringe displacement test was used to measure the flow of the gaseous products. The collection system consisted of a stainless steel vessel to contain the pressure, while a smaller glass vial was contained in the vessel to collect the sample. The glass vial was immersed in ethylene glycol to provide efficient heat transfer to cooling coils external to the collection pot. Temperature of the collection pot was approximately 5°C while the gas space in the pot was held at 8-9°C. The tube run from the reactor to the collection pot was kept as short and vertical as practicable and insulated to minimise product condensation in the line. All tubing was ¼' stainless steel with Swagelok fittings.

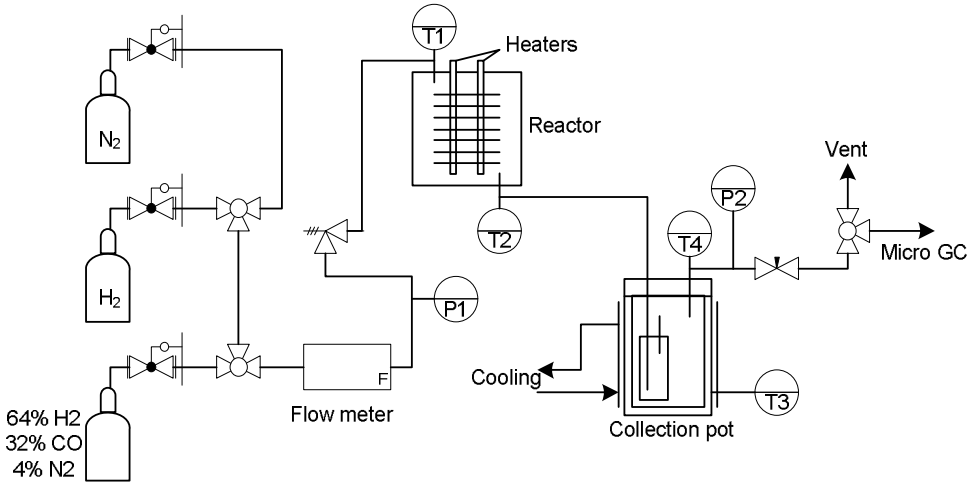

Fig. 3: Schematic of experimental setup

Catalyst addition

A cobalt based catalyst was chosen as the basis for this study. Although the cost is significantly higher than iron the increased activity is seen as critical in supporting the once through process envisioned in the small scale FT system.

Three variations of cobalt catalyst in the microchannel reactor were investigated and the process of washcoating for each is described as follows. The first is an unsupported cobalt washcoat. This was chosen as the simplest form of washcoating to provide a base case for comparison. The second was a cobalt on titania catalyst selected to represent a more typical catalyst supported on a metal oxide. Titania was washcoated followed by cobalt nitrate rather than washcoated together so that the cobalt would have the most active sites exposed to the gas flow through the channel, rather than locked in near the walls. The third method of washcoating was a combustion synthesis form of catalyst. Auto ignition upon heating of the cobalt nitrate/urea mix was intended to quickly form the oxide state and lock in crystal size producing a uniform catalyst with high specific surface area (Ge et al., 2009, Atkinson, 2010). While this method would often have a metal oxide support, the method was trialled without support as a means of comparison to the neat cobalt washcoat.

Neat cobalt

As a means of creating a simple base catalyst for comparison cobalt nitrate without a support was washcoated into the reactor. Temporary transparent tubing was inserted into the feed and outlet ports of the reactor. A solution containing equal weights of DI water and $Co(NO_3)_2.6H_2O$ was injected into the temporary tubing until there was a level in both the feed and outlet tubing.

The reactor was heated to 80°C using the cartridge heaters which were incorporated in the reactor, for 6 hours before ramping the temperature to 400°C for calcination for 5 hours. The mass of cobalt in the channels was estimated from the channel volume and concentration of the cobalt nitrate solution to be 16.4 mg.

Titania supported cobalt

P25 titania (SGE International Ltd) was slurried in DI water to 13% by total mass. The solution was injected into the reactor with temporary tubing as per the other trials. The titania was dried at 80°C.

Cobalt nitrate was then washcoated over the dried titania using a 30% by total mass $Co(NO_3)_2.6H_2O$ in DI water solution. This was again dried at 80°C before calcination for several hours at 400°C. Via calculation, the mass of titania in the channels was estimated at 14.4 mg and the mass of cobalt at 8.3 mg giving a cobalt loading of 37% by total mass.

Combustion synthesis method

Urea was used as the fuel in the combustion synthesis method. The quantity of urea required was calculated based on balancing valencies using methods from propellant chemistry (Castro et al., 1997, Ganesh et al., 2005). A two times mol excess of urea was added to an equal wt DI water and $Co(NO_3)_2.6H_2O$ solution. The solution was washcoated into the reactor by the method described previously. The solution was dried at 80°C for 6 hours before heating to 500°C for auto ignition (temperature ramp and hold time 1.5 hours total), then the temperature was reduced to 400°C for 3.5 hours.

Fixed bed reactor

As a means of comparing the performance of the microchannel reactor with traditional technology a small fixed bed reactor (channel dimensions 4 mm by 6 mm by 30 mm) was fabricated from stainless steel. The fixed bed reactor plate was designed to bolt into the top and bottom reactor plates using aluminium foil gaskets as used in the microchannel reactor. This was done in order to replicate the conditions as closely as possible so that the only variables for comparison were the channel dimensions and form of the catalyst. A simple catalyst using a 12% cobalt loading on titania (P25 SGE international Ltd) prepared by impregnation and freeze drying was used in the reactor. The catalyst was held in the channel by ceramic wool (Kaowool) packing at either end. Approximately 0.4 g of catalyst was packed in the reactor. Temperature programmed reduction (TPR) was performed on this catalyst and showed a typical response for a cobalt catalyst supported on titania with two main absorption peaks (approximately 375°C and 560°C). TPR was also performed on the Kaowool packing blank to ensure there was no interaction from the packing. XRD diffraction pattern analysis gave an estimated cobalt crystal size of 13 nm.

The reduction step for all the catalysts was performed in the same way. Hydrogen was passed over the catalyst at 400 kPa with the reactor ramped to 400°C for 2 hours. While

this reduction time appears short previous experimentation discovered a longer reduction time severely reduced catalyst activity.

Slurry bed reactor

As a further comparison experiments were performed at the Centre for Environmentally Beneficial Catalysis (CEBC) at the University of Kansas in a batch slurry reactor (Parr Instruments 100 mL stirred reactor). A 12% cobalt on titania (Hombikat) catalyst was made via incipient wetness impregnation and a 20% cobalt on alumina was made using a similar method. Calcination, reduction and passivation followed before using in the reactor. Multiple starting pressures and temperatures were investigated and conversion was calculated based on the time it took to drop pressure in the batch reactor. Decane was used as the solvent in the reactor.

Analysis method

Gas products (CO, H_2, N_2, CO_2, CH_4, C_2H_4, C_2H_6) were analysed during the run at regular intervals using an Agilent 300A micro GC. Liquid samples (C_8 to C_{30+} hydrocarbons) were analysed post run in a Varian CP 3800 GC using a Varian Factor Four capillary column (30 m x 0.25 mm ID).

RESULTS AND DISCUSSION

Ease and repeatability of washcoating

Because of the intended use of the washcoats in a simple Fischer-Tropsch system it seems prudent to comment on the ease of catalyst incorporation in the reactor. It should be noted the injection process was chosen as one that could be replicated in a larger scale than the lab scale in use. This is because the coating can be incorporated in a completely assembled reactor. The neat cobalt nitrate and combustion synthesis methods were the simplest to washcoat due to the one step nature of the injection process. Also, as the washcoat precursor is a solution rather than a suspension there were no difficulties with settling while trying to inject the precursor. The combustion synthesised method may be limited in repeatability due to the rapid evolution of gases upon ignition carrying catalyst out of the channels. Visual comparison of the reactor plates upon disassembly would tend to support this hypothesis.

The effectiveness of the slurry injection and drying phases was investigated with the use of a reactor constructed with glass top and bottom plates. This allowed visual observation of the injection and drying processes within the channels. Interestingly, on injection the flow of slurry between channels was very similar indicating the reactor doesn't have a preferential flow path which would effectively reduce residence time. It also demonstrated that with a few cycles of the injection syringe it was possible to remove any air pockets in the channels ensuring an even distribution ready for drying. Of concern was the possibility that during the drying step, water exiting the reactor would cause the support to coat heavier at either end of the channels, while depositing very little support in the middle of the reactor. However, observation of the transparent reactor has shown this not to be a significant problem attributed to the fact that the temperature used for drying was 80-85°C. Keeping the water below boiling temperature minimises the driving force of the liquid leaving the reactor carrying catalyst material with it.

Online performance

The performance of the various washcoats for Fischer-Tropsch synthesis were compared over three temperatures (210°C, 225°C, 240°C) at a pressure of 20 bar. Four runs were conducted for each catalyst in the order of 240°C, 225°C, 210°C, 240°C. The repeat of the 240°C run allowed a comparison of performance between the first and last run after more time on stream and reduction steps.

An important comparison is the performance of the microchannel reactor in terms of conversion to that of the fixed bed reactor. While conversion is often reported as a percentage it was deemed more appropriate to compare conversion in relation to the mass of catalyst in the reactor for two main reasons. 1) Gas Hourly Space Velocity (GHSV) was noted to have little influence on conversion per unit mass of catalyst within the range of flows the equipment would allow and 2) GHSV was adjusted to allow better measurement. i.e. for a catalyst with low conversion the GHSV was reduced to provide a higher fractional conversion allowing more accurate determination of conversion via measurement on the micro GC. GHSV was in the range of 8000-19000 /hr for the microchannel reactors and 1200-2500 /hr for the fixed bed reactor, while CO conversion was in the 5% - 35% range. Note the GHSV was calculated based on the channel volume rather than catalyst volume. No noticable pressure drop was observed over the microchannel reactor at any of the space velocities tested.

However, a challenge to reporting conversion in terms of unit mass of catalyst is the ability to accurately measure the mass of catalyst in the microchannels. Due to the large mass of the microchannel reactor as a complete unit an accurate before and after loading mass measurement is not possible. Therefore the mass in the reactor is calculated as the product of the solution concentration and reactor volume. This method relies on the assumption that the channels are full, and upon drying, the catalyst precursor solution dries and deposits without either concentrating in the channels or evacuating from the channels. The system was run for at least 5 hours to reach steady state before calculating conversion.

Conversion in terms of gram of C_{2+} product per gram of catalyst per hour is shown in Table 1 and was calculated based on CO consumption and stoichiometry. The microchannel reactor in all cases is operating with significantly higher activity (up to 40 times) than a more traditional fixed bed arrangement. Literature survey yields comparable results. Cao (2009) reports productivities up to 1.7 gC_{2+}/g catalyst/hr at 224 °C and 25 bar. This was based on a powdered Co/Re catalyst supported on alumina packed in the microchannels. This research at 225°C and 20 bar yields a maximum productivity for the neat cobalt washcoat of 2.2 gC_{2+}/g catalyst/hr. Myrstad (2009) investigated a slightly different type of micro reactor incorporating pillar structured catalyst foils, however, like Cao (2009) the catalyst was packed into the reactor and was Co promoted with Re on an alumina support. At 240°C the gC_{5+}/g catalyst/hr productivity was 2.6, while at 225°C productivity was 1.7 gC_{5+}/g catalyst/hr. This research compares with 5.7 and 1.6 gC_{5+}/gcatalyst/hr respectively with the neat cobalt washcoat. Given the lack of precious metal promotion used in this research the productivity per unit catalyst results are encouraging.

Catalyst activity was very dependent on temperature and activity followed a logarithmic trend in relation to temperature, as is expected with typical reaction kinetics. Temperature, however, appeared to have a more dramatic affect on productivity compared to that reported in the research by Myrstad (2009).

Tab.1: Product conversion (gC_{2+} products/g catalyst/hr) over temperature range for various washcoats

	240°C	225°C	210°C	240°C
Cobalt	7.4	2.2	1.4	3.6
Cobalt on titania	2	0.8	0.54	1.3
Combustion synthesis	2.5	0.61	0.67	1.8
Fixed bed	0.19	0.067	0.04	0.12

Comparison of the various microchannel washcoats showed the simplest method of neat cobalt nitrate to be the highest performing coating in terms of conversion per unit of catalyst. It was hypothesised that the titania supported method would yield the highest performing catalyst due to the expected extra surface area. Even on comparison of conversion per actual Co loading (rather than total catalyst mass) the neat Co still outperformed the titania supported catalyst. From comparison of SEM results one possible conclusion is that the microfiber and jagged mountain geometry generated in the neat cobalt washcoat provided sufficient surface area to be comparable or better than what the titania supported catalyst could afford. If different loading concentrations were investigated it would be interesting to note if there is a changeover point at which the titania supported method would out perform the neat cobalt. With the high loading the neat cobalt is providing its own high surface area support. At lower loadings this may not have such an effect and cobalt spread over the high surface area titania may be more advantageous. However, while it has been termed 'high loading' there is still very high activity per unit catalyst requiring little catalyst for conversion compared to traditional technology. Therefore, it is seen as being no advantage to try and significantly reduce the catalyst in the channels. Rather it is considered beneficial to maximise as much as possible the active sites within the microchannels, even at the expense of catalyst utilisation efficiency. On this premise, if pure cobalt is its own best high surface area support, then this should be pursued. One question of the unsupported washcoats will be their resistance to deactivation over significant run periods, which are not achievable within the current laboratory setting.

Results were fitted to an Anderson-Shultz-Flory (ASF) distribution to determine the selectivity (α). The most accurate fit was possible in the C_8 to C_{22} range particularly in the 240°C runs where higher activity resulted in a greater quantity of sample. This is within the fuels range so the most accurate analysis is within the range of interest. With the higher weight hydrocarbons there is a drop off from the expected mass fraction which is attributed to product drop out in the collection pot feed, however, this does not affect identification of a suitable product distribution.

An approximation for α in relation to temperature from Song (2003) yields 0.77 for 240°C, 0.81 for 225°C and 0.85 for 210°C. Selectivity varied significantly from these predictions as can be seen in Table 2. Selectivity in most cases trended opposite to typical FT prediction in relation to temperature. Some of this may be attributed to error, especially at the lower temperatures where less activity resulted in less product. However, due to the accuracy at which the 240°C runs fit the ASF distribution one can assume an accurate value. This is an encouraging result as the α value in the mid 0.8's is much higher than predicted at that temperature and is an appropriate range for high fuel production, while operating at a higher temperature and therefore increased catalytic activity. Comparing results to Cao (2009) who achieved an average α of 0.87 at 225°C this research is shown to be in a similar range. Methane selectivity as seen in Table 2 could be considered on the high side, particularly at the higher temperature of 240°C,

however, it was very consistent over all the different washcoats in the microchannel reactor. Surprisingly the fixed bed reactor exhibited the lowest methane production. Note the %CO converted to methane is not shown at 210°C due to low activity at this temperature not producing enough methane to register on the microGC.

Tab.2: Values of α and % of converted CO converted to methane over temperature range

	240°C		225°C		210°C		240°C	
	α	%CO to CH_4	α	%CO to CH_4	α	%CO to CH_4	α	%CO to CH_4
Cobalt	0.83	21	0.74	16	0.72	n/a	0.83	20
Cobalt on titania	0.82	21	0.73	15	0.64	n/a	0.77	22
Combustion synthesis	0.89	21	0.84	16	0.87	n/a	0.71	17
Fixed bed	0.87	17	0.85	10	0.84	n/a	0.89	15

Tab.3: Product distribution (mass %) for various catalysts over temperature range calculated from α

	240°C		225°C		210°C		240°C	
	C_5-C_{19}	C_{20+}	C_5-C_{19}	C_{20+}	C_5-C_{19}	C_{20+}	C_5-C_{19}	C_{20+}
Cobalt	68	12	59	1.9	56	1.2	68	12
Cobalt on titania	68	9.0	58	1.6	41	0.16	64	3.7
Combustion synthesis	58	27	67	13	63	22	53	0.86
Fixed bed	63	22	67	15	67	14	57	29

Table 3 shows in most cases the product distribution was quite favourable for fuels production. Again one must remember the application of this technology is small scale, localised F-T. It is anticipated the F-T syncrude would be transported to a central refinery, however, if a significant fraction is within a useable fuel range then some simple separation on site may be a suitable option. Separation would especially focus on diesel fuels due to the high need for diesel in the local forest industry, and due to the high quality of diesel available from the FT process (Dry, 2002).

The work performed in the CEBC at The University of Kansas provided a useful comparison of a different reactor technology. While there wasn't sufficient experimental time to optimise the experimental method, initial results showed the catalyst performance in the batch slurry system to be similar to that in the fixed bed reactor at the University of Canterbury. Similar trends in activity to temperature between the two systems affirmed the reliability of the control and measurement for the in house built Univeristy of Canterbury system when compared to that of a reputable supplier (Parr Instruments).

CONCLUSIONS

A microchannel reactor was constructed to allow comparison of various types of washcoating of Fischer-Tropsch catalysts, as well as comparison with a fixed bed reactor and powdered catalyst. The microchannel reactor was found to function at productivities per unit of catalyst 32 to 40 times higher compared to the fixed bed reactor. The productivities of the washcoated catalysts were also comparable to other microreator FT work in literature using packed beds (Cao et al., 2009, Myrstad et al., 2009). Experimental research established that a simple washcoat of unsupported cobalt

was the most effective catalyst in terms of productivity. Temperature was also shown to have a significant influence on productivity. In addition at higher temperature (240°C) product selectivity was found to be still within a range suitable for fuels production. Therefore it can be concluded in a small scale combined heat, power and fuel plant with a once through arrangement the process should be run at this higher temperature to maximise productivity per unit catalyst. In this scenario the benefits of higher temperature and productivity should outweigh any disadvantages in terms of product selectivity.

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